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INFRARED ABSORPTION OF INHOMOGENEOUS MEDIA WITH METALLIC INCLUSIONS

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Invited paper

The absorption of far infrared radiation by small metal particles and metal-insulator composite materials is reviewed. The possibility of observing quantum size effects is examined. Recent experimental and theoretical progress in understanding the anomalous enhancement of the far infrared absorption coefficient is discussed.

1. Introduction

This paper briefly reviews the present understanding of the interaction of far infrared (FIR) radiation with small metal particles and metal–insulator composite materials. The important issues of quantum size effects (QSE), the anomalous enhancement of the far infrared absorption coefficient, and other recent activity are discussed. This paper is an update to several more detailed reviews [1–4] of this topic.

2. Quantum size effects

Interest in the far infrared absorption by small metal particles was initially motivated at least in part by the possibility of observing transitions between discrete levels. The effects of confinement on the energy levels of the conduction electrons in a particle can be described by quantum box models, as first discussed by Fröhlich [5] and later refined by others [6–10]. The levels calculated in these models tend to have a high degree of degeneracy due to the assumed symmetry of the particle (usually a cube or sphere). Details in the optical structure predicted by these models are not presently observable due to imperfections in the shapes of particles, surface roughness, and the inevitable distribution of sizes.

Kubo [11] introduced a statistical approach to QSE's in ultrafine metal particles. He estimated the level spacing at the Fermi energy E_F of a particle by

inverting the density of electron states at E_F for a given spin to obtain the "Kubo gap" $\delta = 4E_F/3nV$, where n is the density of free carriers and V the volume of the particle. Using free electron values, δ is on the order of $10\,cm^{-1}$ (1 meV) for typical metals (Al, Ag, Au, Cu, ...). An exceptionally large δ is predicted for Bi particles [12].

Gor'kov and Eliashberg (GE) [13] asserted that Kubo's use of the Poisson distribution to describe the level statistics neglects correlations between the levels. According to GE, the randomness of the level distribution in an ensemble of metal particles introduced by surface roughness is described by the statistical theory of levels (random matrix theory) originally developed by Wigner [14], Dyson and Mehta [15], and others for applications in nuclear physics. After corrections for a number of errors in the original paper [16–18], the GE model predicts oscillations in the frequency dependence of the FIR absorption coefficient superimposed on a quadratic background. When account is taken of the particle size distribution present in actual samples, the signatures of QSE's disappear [18]. At present no evidence has been obtained for QSE's in small metal particles by a far infrared experiment. Thus, theory and experiment are presently in agreement, but a rigorous test of the theory requires the ability to manufacture particles with a very sharp size distribution.

Devaty and Sievers [19] reexamined the possibility of observing QSE's by absorption spectroscopy and found reduced absorption for frequencies below the mean Kubo gap. The effect is weak, but persists even in the presence of a size distribution.

An anomalously low microwave conductivity recently observed [20] for small indium particles dispersed in oil has been interpreted as evidence for a QSE [21] using the GE model.

Shklovskii [22] discussed a modification to GE's argument based on electron–electron interactions and concluded that the frequency dependence of the FIR absorption coefficient predicted by GE must be reduced by a factor of $\hbar\omega/\delta$.

Random matrix theory has been an active area of research recently [23]. Efetov [24] derived the two-level correlation functions for Dyson's three circular ensembles using the mathematics of supersymmetry. Several groups have questioned the assumptions underlying the GE model [25–28], particularly whether randomness introduced by boundary conditions can be described by random matrices. The issue appears to be unresolved at this time.

3. The anomalous far infrared absorption

Most measurements of the far infrared absorption coefficient of small metal particles imbedded in an insulating host have been performed on samples

having a low metallic volume fraction f. In the limit of low f, long wavelength, and assuming that the particles are randomly dispersed, the predictions of effective medium theories reduce to a simple expression which can also be obtained from the Mie–Debye solution for a single sphere. For a Drude metal particle imbedded in a nonabsorbing host, with the bulk relaxation time replaced by v_F/a (v_F = Fermi velocity, a = particle radius), the FIR absorption coefficient α reduces to the sum of electric (ED) and magnetic (MD) dipole terms with the properties: (1) quadratic frequency dependence, (2) size dependence: $\alpha_{ED} \sim a^{-1}$ and $\alpha_{MD} \sim a^3$, (3) for a typical metal, say Al, the MD term dominates for diameters greater than 50 Å.

An enhancement of one to four orders of magnitude in the FIR absorption coefficient of small metal particles and metal–insulator composites with respect to theoretical predictions was discovered by Tanner et al. [29] and subsequently characterized [30–33]. The samples under study were typically particles prepared by inert gas evaporation [34], sometimes in the presence of O_2 to produce an oxide coating, and dispersed in an alkali halide host by repeated grinding and pressing into pellets. Free-standing particles (smokes) were also examined. The principal results are the ubiquity of the enhancement (observed for Al, Ag, Au, Cu, Pd, Sn, and Pt), an approximately quadratic frequency dependence, and a linear dependence on f for small f (with the exception of Al [33]). In addition to the enhancement, the far infrared properties of superconducting particles showed anomalous behavior in the region of the gap [35].

A number of mechanisms were proposed in attempts to explain the anomalous absorption. Mechanisms intrinsic to isolated particles include vibrations [36, 37], eddy currents and nonlocal effects [38–40], particle size distributions [41], Coulomb effects [42], and quantum size effects [43]. Mechanisms for enhancements induced by clustering include oxide-coated clusters [44, 45], eddy current losses [46], and geometrical effects (shape, close approach of spheres) [46]. These mechanisms do not explain the enhancement in a satisfactory manner, either because the experimental result is larger than theory or because the proposed explanation is too specific to cover all the experiments.

An experimental breakthrough occurred with the realization of the importance of well-characterized samples with controllable properties to distinguish among proposed mechanisms. Devaty and Sievers [47] developed a novel composite material, ~100 Å Ag particles supported in gelatin, that could be sectioned with an ultramicrotome for examination by transmission electron microscopy as well as pressed into pellets for FIR measurements. Samples could be prepared with the particles well dispersed or deliberately agglomerated. Studies of this material provided evidence for the important role of clustering to the enhancement. Bounds were placed on the magnitude of the enhancement for dispersed particles (absorption by the gelatin dominated

absorption by the particles). Deliberate clustering produced an increase in absorption.

Additional experiments provided further important clues. Curtin et al. [48] showed that a heat treatment (melting the particles) eliminated the anomalous behavior of superconducting Sn particles near the gap. This experiment motivated the models of Curtin and Ashcroft [49], which provide an explanation for the enhancement. Lee et al. [50] introduced a new host, DLX-6000, a teflon-like material, which can be ultramicrotomed for electron microscopy but, unlike gelatin, is a weak FIR absorber. They studied fairly large Ag particles imbedded in teflon and were able to obtain agreement with theory for dispersed particles and demonstrated enhanced absorption for a clumped sample.

The results of these experiments directed theorists to focus on clustering as a mechanism for enhanced FIR absorption. Curtin and Ashcroft [49] introduced three different models. In the fused cluster model, a dense cluster is modeled as a metallic sphere with a scattering time determined by the radius of an individual particle. The short relaxation time leads to enhanced eddy current (MD) absorption. The cluster percolation model treats a cluster as a sphere made up of an effective medium. The sample is modeled as a dilute mixture of clusters which make up a second effective medium. Enhanced absorption occurs for clusters with f near the dc percolation threshold f_c; i.e., there is a resonance in f. The enhanced ED absorption is caused by the tortuous, poorly conducting clusters near f_c. Although Curtin and Ashcroft modeled their cluster using a treatment based on the real space renormalization group, any effective medium theory with a percolation threshold should do the job, at least qualitatively. Perhaps the simplest approach is to model the clusters using the Bruggeman model [51] and use the Maxwell-Garnett model [52] to average over the clusters. The third model, the cluster–tunnel junction model, applies to closely spaced oxide-coated particles in clusters. The absorption mechanism is photon-induced electron transfer. Hui and Stroud [53] modeled a cluster using a self-similar effective medium theory [54] and examined a possible role for tenuous fractal clusters in the enhanced absorption. Niklasson et al. [55] also examined fractal clusters. Claro and Fuchs [56] modeled clusters of particles by introducing a distribution of effective depolarization factors. They obtained an enhancement of 3–4 orders of magnitude in the FIR ED absorption.

In addition to clustering, recent theoretical work has considered other mechanisms including surface phonons [57], electron–phonon coupling [58], diffuse surface scattering [59], relaxation time effects [60], and quantum size effects [61].

Recent experimental work in the far infrared has focussed on new issues.

Previous studies at low teperature ($T < 20$ K) showed no evidence for temperature dependence in α. Noh et al. [62] have measured the temperature dependence of α for a Ag–teflon composite from room temperature down to liquid He temperatures and observed a small (~10%) effect. They found satisfactory agreement with a model which included the effects of oxide coats, particle size distribution, and modification of the electronic relaxation time due to impurities within the particles. Lee et al. [50, 63] showed that oxide coatings lead to enhanced absorption in the mid and far infrared. Sherriff and Devaty [12] have studied the unusual FIR properties of Bi particles. Kuroda et al. [64] have measured FIR absorption by small particles of the high-T_c superconductor $YBa_2Cu_3O_{6.74}$. Sievers' group [65] applied the Bruggeman model [51] to FIR data on sintered pellets of high-T_c superconductors and related compounds.

The role of clustering in the anomalous enhancement of the FIR absorption coefficient appears to be understood. However, there are some unresolved issues. The dependence of α on particle size has not been systematically studied. The inevitable size distributions make such a study difficult, but theoretical predictions should be tested experimentally. In addition, there have been few FIR studies of metal–insulator composite materials over a large or complete range of composition [66]. Such studies, which might focus on the region of dc percolation, would test effective medium theories and extend similar studies in the IR–vis–UV into a new spectral region.

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